

B3

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

EP 0 607 703 B1

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention  
of the grant of the patent:

06.05.1998 Bulletin 1998/19

(51) Int Cl<sup>6</sup>: C08F 10/00, C08F 4/609

(21) Application number: 93310588.4

(22) Date of filing: 29.12.1993

(54) **A prepolymerized catalyst composition, a process for the preparation thereof, and a process for polymerizing alpha-olefins**

Prepolymerisierte Katalysatorzusammensetzung, Verfahren zu seiner Herstellung und Verfahren zur Olefinpolymerisation

Composition catalytique prépolymerisée, procédé pour sa préparation et procédé de polymérisation d'oléfines

(84) Designated Contracting States:  
BE DE FR GB IT SE

• Leskinen, Pauli  
F-00800 Helsinki (FI)

(30) Priority: 29.12.1992 FI 925913

(74) Representative: Pawlyn, Anthony Neil  
Urquhart-Dykes & Lord,  
Tower House,  
Merrion Way  
Leeds, West Yorkshire LS2 8PA (GB)

(43) Date of publication of application:  
27.07.1994 Bulletin 1994/30

(73) Proprietor: BOREALIS A/S  
2800 Lyngby (DK)

(56) References cited:  
EP-A- 0 083 074 EP-A- 0 260 647  
GB-A- 1 309 467 LU-A- 61 371  
US-A- 4 235 747

(72) Inventors:

• Pentti, Ismo  
F-06850 Kulloo (FI)

EP 0 607 703 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**Description**

The present invention concerns a prepolymerized catalyst composition suitable for use in the polymerization of alpha-olefins and a process for preparing such a composition. The invention also relates to a process for polymerizing 5 alpha-olefins with a Ziegler-Natta catalyst composition, according to which a procatalyst composition comprising a transition metal is prepolymerized with a monomer for producing a Ziegler-Natta type prepolymerized catalyst composition and this catalyst composition is contacted with an alpha-olefin monomer in order to produce a polymer.

Ziegler-Natta catalysts have been used for a long time for stereospecific polymerization of alpha-olefins. In their broadest sense Ziegler-Natta catalysts comprise a compound, usually a halide, of a transition metal of groups IV to 10 VIII of the periodic system together with a cocatalyst comprising an alkyl derivative of a group I to III metal. Titanium chlorides are representatives of typical transition metal compounds used, and of the metal alkyl compounds aluminium alkyl derivatives should be mentioned. Often a Ziegler-Natta catalyst also contains an electron donor, such as a Lewis base, the purpose of which is to render the polymerization product more isotactic. In order to improve the catalyst's activity, its surface is increased by adding the catalyst onto a support. The most common support is magnesium dichloride. 15

The activity of supported catalysts (calculated on basis of the weight of the transition metal) can be up to 100 times higher than the activity of unsupported catalysts. This is the reason why a growing interest is being focused on these catalysts. Supported Ziegler-Natta type catalysts can be prepared by depositing a transition metal compound, such as 20 titanium tetrachloride, on a support, and then reducing the transition metal compound with an organic metal compound acting as a cocatalyst either before polymerization or at the beginning of polymerization. The deposited support is often dried before being subjected to reduction, but polymerization and reduction of the transition metal can be carried out directly after deposition of the catalyst on the support, which makes it possible to omit the drying step. This alternative is preferred if the supported catalyst is to be posttreated by prepolymerizing a suitable monomer on its surface, which 25 is the case in, for instance, bulk polymerization of propene, wherein the catalyst is prepolymerized before being added into the polymerization reactor.

According to conventional technology, the Ziegler-Natta catalyst is used for polymerization in particulate form. In order to facilitate catalyst dosing the catalyst can be combined with wax which makes it possible continuously to feed a prepolymerized wax catalyst into the polymerization reactor. By way of example, reference is made to GB Patent Application No. 2,189,252, which anticipates a catalyst for the polymerization of 1-alkenes. Said prior art catalyst is 30 prepared by depositing transition metal compounds on silica or alumina, a paraffinic hydrocarbon being applied to the catalyst together with a transition metal compound or to the completed catalyst. The paraffinic hydrocarbon can be prepared by prepolymerization of a small amount of 1-alkenes on the support.

The handling of wax catalysts is uncomplicated and safe during the various stages of the process. An additional benefit associated with wax protected catalysts resides in the fact that the catalyst is not as easily destructed by external 35 catalyst poisons as conventional catalysts. However, as a disadvantage, it should be noted that the process for preparing the wax catalysts comprises several stages; according to the prior art, the catalyst particles will first have to be dried before they can be mixed with the wax, in which they are prepolymerized. The GB Patent Application No. 2,189,252 mentioned above indicates that the solvent used during the addition of the wax has to be removed, e.g., by decantation, by evacuation or by evaporation.

40 The preparation reactions and the reactants of the Ziegler-Natta-catalysts are extremely sensitive to impurities. In particular, the drying of the catalyst is a sensitive stage during which the catalyst may easily be deactivated. For this reason there have been developed processes which comprise conducting the activation, washing, drying and prepolymerization stages in the same apparatus. In this context, reference is made to the equipment described in the U.S. Patent Specifications Nos. 5,137,551 and 5,215,949. Said references do not, however, deal with the preparation of prepolymerized catalysts which are fed in wax.

EP-A-0083074 provides an ethylene polymerisation catalyst. However the oil added to disperse the catalyst composition is of a low viscosity, the catalyst composition being added thereafter to a low viscosity aliphatic hydrocarbon. The low viscosity of this composition inevitably leads to settling of the catalyst during storage for instance.

US 4235747 relates to a method for synthesising a catalyst rather than to prepolymerising a catalyst composition. 50 This prior art catalyst is also subject to settling out from its formation mixture upon standing.

It is an aim of the present invention to eliminate the disadvantages of the prior art while providing an entirely novel prepolymerized Ziegler-Natta catalyst composition and a process for the preparation thereof. The invention also aims at providing a novel process for polymerization of alpha-olefins with the help of Ziegler-Natta catalysts mixed with wax.

The invention is based on the concept of combining the preparation of the prepolymerized wax catalyst with the 55 activation of the catalyst. The last drying stage of the catalyst activation is then entirely left out and the prepolymerization of the wax catalyst is carried out after activation in a viscous medium.

According to the invention we provide a prepolymerized catalyst composition suitable for use in the polymerization of alpha-olefins, comprising a prepolymerization medium comprising a procatalyst composition comprising a transition

metal, the procatalyst composition being prepolymerized with a prepolymerization monomer in the presence of a viscous substance, the viscosity of the viscous substance being such that the prepolymerization medium viscosity is at least 1 Ns/m<sup>2</sup> (1,000 cP). The medium used for prepolymerization may comprise a substance which is inert to the catalyst components and which has a viscosity suitably high for preventing the catalyst from settling in this medium during transport or storage. Within the scope of the present invention, this substance is called "a viscous substance". Typically, the viscosity of such a medium is in the range of 1 Ns/m<sup>2</sup> to 15 Ns/m<sup>2</sup> (1,000 to 15,000 cP), preferably 4 Ns/m<sup>2</sup> to 10 Ns/m<sup>2</sup> (4,000 to 10,000 cP).

More specifically, the catalyst composition according to the invention is characterized in that it comprises a transition metal prepolymerized with a prepolymerization monomer in the presence of said viscous substance.

The process according to the invention for preparing a prepolymerised catalyst composition suitable for use in the prepolymerisation of alpha-olefins, comprising:

- (a) forming a procatalyst composition by depositing a transition metal compound on a suitable support,
- (b) adding said procatalyst composition to a viscous substance;
- 15 (c) prepolymerizing said procatalyst composition with said prepolymerization monomer in the presence of said viscous substance to provide a prepolymerization medium and so to obtain said prepolymerized catalyst composition, the viscosity obtain said prepolymerized catalyst composition, the viscosity of the viscous substance being such that the prepolymerization medium viscosity is at least 1Ns/m<sup>2</sup>.

Within the scope of the present application, the term "procatalyst" denotes a transition metal compound suitable for a Ziegler-Natta catalyst, containing the metal in reduced or reducible form. The term "procatalyst composition" means, again, a composition donors and other similar additional components.

The transition metal compound of the procatalyst composition can comprise compounds of different kinds. The most usual are titanium compounds - organic or inorganic - having an oxidation degree of 3 or 4. Of the other transition metals, vanadium, zirconium, chromium, molybdenum, cobalt, nickel, tungsten and many rare earth metals should be mentioned. The transition metal compound is usually a halide or oxyhalide, an organic metal halide or purely a metal organic compound. In the last-mentioned compounds, there are only organic ligands attached to the transition metal. Particularly preferred transition metal compounds are selected from the group comprising halides of titanium, in particular TiCl<sub>4</sub>, and titanium alkoxides and alkoxy halides. The following examples of other suitable compounds can be mentioned: vanadium trichloride, triacetyl acetone vanadinium and triacetyl acetone chromium, cobalt chloride-pyridinium complexes, dichorodicyclopentadienyl titanium.

According to the invention, a supported catalyst composition is prepared, wherein the support mainly is inert, i.e., it does not affect the polymerisation reaction in itself. However, when the catalyst particles are deposited on the surface of a support having a large surface, the monomer molecules are more readily polymerized. The support is either an organic compound (e.g. a polymer) or an inorganic compound, such as a metal oxide. The following inorganic compounds may be mentioned: silicon dioxide, aluminium oxide, Ti, Mg, Cr, Ba, Th and Zr oxides, silicates, halides, such as CaCl<sub>2</sub>, and in particular magnesium halides, the most important of which is MgCl<sub>2</sub>. The inorganic support can also be a metal hydroxide or a metal hydroxy halide. Combinations of various supports are possible, as well. Typical support combinations are silica and magnesium dichloride and cogels of silica and other oxides.

During "prepolymerization" the procatalyst composition is contacted with a monomer in the presence of a cocatalyst and possibly an (external) electron donor, the monomer being polymerized on the surface of the composition.

The cocatalysts conventionally used are comprised of aluminium compounds, but compounds of lithium, sodium and potassium, alkaline earth metals as well as compounds of other earth metals than aluminium are possible. The compounds are usually hydrides, organometal or halide compounds. Conventionally, the cocatalysts are selected from the group comprising Al-trialkyls, Al-alkyl halides, Al-alkoxides, Al-alkoxy halides and Al-halides. In particular, Al-chlorides are used. These compounds are exemplified by triethyl aluminium, ethyl aluminium chloride, ethyl aluminium dichlorides and aluminium trichloride. Butyl lithium and butyl magnesium jodide are examples of useful compounds of other metals.

As mentioned above, Lewis base type donors known *per se* can be used for improving the stereospecificity of the catalyst. The donors are divided into two cathegories depending on whether they are added to the mixture of the transition metal compound and the support (internal donors) or to the mixture of the monomer and the catalyst component (external donors). Donors of both kinds can, of course, be added to the catalyst system, for instance by first preparing a procatalyst composition by way of depositing the transition element on the support in the presence of an internal donor, and then reacting the procatalyst composition with the monomer, a cocatalyst and an external donor being added to the polymerization mixture. The internal and external donors can be identical or different, the main donor types being represented by ethers, esters, carboxylic compounds, ketones, amines, amides, phosphines, organophosphorous compounds and polymer derivatives. In the examples below, ether compounds have been used as external donors.

According to the invention the procatalyst composition is prepolymerized with a suitable monomer in the presence of a polyolefinic wax in order to produce a prepolymerized catalyst composition. Within the scope of the present invention, the term "catalyst composition" denotes a composition which, in addition to the components of the procatalyst composition, contains a cocatalyst and possibly an external donor and which can be used for polymerization of olefins.

5 Any suitable monomer with unsaturated bonds can be used for prepolymerization. Particularly suitable monomers are 1-olefins, such as ethylene, propene, butene, 4-methylpentene and vinylcycloalkanes, in particular vinyl cyclohexane. Mixtures of monomers can be employed in prepolymerization, and prepolymerization monomers can be combined also by changing the monomer in the middle of the prepolymerization.

10 Often, a chain transfer agent suitable for regulating the molecular weight and the molecular weight distribution of the polymer product produced can be used for prepolymerization. As chain transfer agents, different metal organic compounds, such as alkyl Zn compounds, or hydrogen, can be employed. Hydrogen is a typical and preferred alternative, because it does not leave any foreign atoms in the polymer.

15 It should be pointed out that the same or different monomer can be applied for prepolymerization as for the production of the actual polyolefin product.

20 According to the invention different oils and waxes having a sufficiently high viscosity can be used as viscous substances. As mentioned above the viscosity of the selected medium should be at least 1 Ns/m<sup>2</sup> (1,000 cP). The medium should furthermore be inert with respect to the components of the catalyst which is being prepared and it must be suitable for dosing of the catalyst. Thus, there should be no additives, such as stabilizers, present in the medium which could act as catalyst poisons, nor should there be polar groups, which may interfere with polymerization. Of the suitable high-viscosity oils, different synthetic poly- $\alpha$ -olefin oils should be mentioned in particular. The molecular weight of said oils are typically in the range of 400 to 1,000, and their viscosity numbers exceed 70.

25 According to a preferred embodiment of the invention the medium used for feeding the catalyst comprises a viscous substance which preferably is comprised of a polyolefin-based mixture, in particular a polyolefin, preferably polyethylene or atactic polypropene, dissolved in a poly- $\alpha$ -olefin oil (PAO) or mixed therewith. Typically, the polyolefin concentration of a mixture of this kind amounts to 1 to 50 %, preferably 1 to 25 % of the weight of the PAO. Also other viscous compounds can be used, provided they meet the above requirements regarding the functional groups and additives.

30 According to a preferred embodiment of the invention, the prepolymerization is carried out as follows (it should be noted that the indicated procedure can, *mutatis mutandis*, be used for other viscous compounds):

The wax used is prepared in a prepolymerization reactor. Alternatively, it is prepared in a separate reactor and then afterwards fed into the prepolymerization reactor. During wax preparation due care is taken to produce a wax with so high viscosity that no settling takes place after prepolymerization; the process aims at getting the catalyst evenly distributed throughout the wax, and the catalyst should remain well distributed during storage. Too high a viscosity renders the even distribution of the catalyst more difficult during reaction. Typically the viscosity of the wax is kept in the above-mentioned range from 4 Ns/m<sup>2</sup> to 10 Ns/m<sup>2</sup> (4,000 to 10,000 cP).

35 After preparation, the wax is cooled to 10 to 40 °C, typically to 20 to 30 °C before the procatalyst composition is added. The procatalyst composition can be introduced into the wax together with an external donor and with a cocatalyst. An inert solvent, such as pentane, is preferably used as a medium during the addition of the components. A procatalyst composition comprising the cocatalyst, the electron donor and procatalyst composition is then formed in said inert solvent, for instance in pentane, and the procatalyst suspension is introduced under mixing into the wax which contains the cocatalyst. The procatalyst composition can, however, also be added into the wax separately from the donor and the cocatalyst without being mixed with any medium. The procatalyst is introduced into the wax below the surface of the wax and the wax-catalyst-composition is mixed after the introduction for some time (for instance for 1 to 120 min.) in order evenly to distribute the catalyst composition within the wax. Preferably the procatalyst composition is fed into a mixed zone of the wax. If desired, a portion of the donor and the cocatalyst can also be separately or jointly mixed into the wax before the catalyst and the rest of donor and the cocatalyst are added. As far as the invention is concerned, it is essential that the catalyst be fed into the wax or similar viscous medium, because otherwise inhomogeneous lumps might easily be formed on the surface of the medium during prepolymerization. Mixing and stirring is also important as regards the production of a homogeneous product.

40 A predetermined amount of a monomer is introduced into the mixed combination of the medium and the catalyst. Typically 0.01 to 50 g, preferably 0.1 to 10 g, of the monomer are added for each gram of the catalyst. The monomer is also fed below the surface of the wax and the agitation is continued until all the monomer substantially has been consumed. During the introduction of the gaseous monomer an increased monomer pressure is preferably maintained. The reaction can also be carried out in an inert atmosphere, a part of the increased pressure being produced with the inert gas. The temperature is maintained as even as possible during prepolymerization.

45 55 After the reaction the prepolymerized catalyst composition can be removed from the reaction vessel and used for polymerization. It has been found to have an excellent shelf life.

Summarizing the above-described features, the essential steps of the particularly preferred steps process are:

- preparing a wax having a viscosity in the range of 4 Ns/m<sup>2</sup> to 10 Ns/m<sup>2</sup> (4,000 to 10,000 cP) in a reaction vessel,
- maintaining the temperature of the wax at 10 to 40 °C,
- mixing a cocatalyst for the procatalyst composition and an electron donor with said wax to produce a cocatalyst-containing wax composition,
- 5 - adding the procatalyst composition and the monomer used for prepolymerization of the procatalyst composition to the cocatalyst-containing wax, and
- prepolymerizing the procatalyst composition until the monomer has been essentially consumed.

10 The catalyst composition according to the invention can be used for polymerization of  $\alpha$ -olefins, such as ethylene, propene, butene, in particular ethylene or propene or mixtures thereof in manners known *per se*.

15 The invention provides considerable advantages. Thus, when the process according to the invention is implemented, the catalyst does not have to be dried before being fed into the medium and, as a result, a high catalyst activity is maintained. Furthermore, the catalyst does not need to be removed from the reactor, transferred into product containers and weighted separately before being introduced into the prepolymerization reactor. This means that several process 20 and work steps become completely superfluous. The amount of waste is also diminished, because the prepolymerization medium does not have to be removed.

Surprisingly it has been found that the properties of the prepolymerized catalyst are not impaired by carrying out the prepolymerization in a viscous medium. Nor are the properties of the polyolefin prepared in the presence of a catalyst according to the invention. In both cases, the results obtained are fully comparable with the properties of 25 products prepared by conventional techniques. The viscous substance has not been found to impair the properties of a product prepared by continuous bulk or slurry polymerization in equipment on pilot plant scale.

The are no up-scaling problems when moving from laboratory scale to pilot plant or industrial scale.

Next, the invention will be described in more detail with the help of a couple of working examples. The examples 25 describe prepolymerization of catalyst compositions in a polyolefin wax and the use of a catalyst composition thus produced for preparing polyolefins, which represents a particularly preferred embodiment of the invention. It is clear to a person skilled in the art that the concept of the invention can also be implemented by suitably altering the specific details of the working examples with the aid of other kinds of waxes and similar viscous substances and other kinds of catalyst compositions, as mentioned above.

30 The activity of the prepared catalysts was determined by bulk polymerization of propene according to the following standard procedure:

#### **Test polymerization:**

35 The monomer (propylene) is purified before polymerization with aluminium oxide and with three purification catalysts. The purification catalyst used comprised a reduced BASF R 3-11 copper catalyst and 3 Å (1 Å = 0.1 nm) and 10 Å molecular sieves, respectively.

The polymerization was carried out in a 2 dm<sup>3</sup> laboratory autoclave equipped with a stirrer. 900 ml of heptane was first fed into the reactor as polymerization diluent. The heptane is purified with the same kind of purification catalysts as the monomer and it is kept in an autoclave under nitrogen pressure.

40 In a separate vessel, 30 ml of heptane, 680 µl triethylaluminium (TEA) and about 50 µl of cyclohexyl methyldimetoxy silane (CHMMS) are then taken, and these substances are reacted with each other for about 5 min with intermittent stirring. Then 15 ml of TEA-donor-heptane solution is taken from the vessel and added upon the catalyst on a septum flask which, with the suspension formed, is agitated. The rest of the TEA-donor-heptane solution is fed into the reactor. The catalyst suspension is carefully introduced into the reactor and polymerization is then initiated by first feeding 45 hydrogen into the reactor and then propylene at the same time as the temperature is increased. The pressure is allowed to raise to up to 7 bar and the temperature to 70 °C within 15 minutes. The rotational speed of the stirrer should be increased to 600 l/min. The polymerization is continued for 4 h.

After the reaction the polymer is separated from the liquid phase by filtering.

#### **50 EXAMPLE 1**

##### **Prepolymerization of a MgCl<sub>2</sub> based catalyst with propylene on laboratory scale**

A PP catalyst of Ziegler-Natta type which had been prepared according to Finnish Patent No. 86866 was prepolymerized in a 2.0 dm<sup>3</sup> reactor. A mixture containing 15 wt-% of atactic polypropylene (APP) and PAO oil (Neste Oy Nesbase 2006 FG) was used as reaction medium. The mixture was first prepared in a prepolymerization reactor. The temperature of the mixture was decreased to + 25 °C, the viscosity being 5.7 Ns/m<sup>2</sup> (5700 cP).

Reagents used:

- Catalyst 20 g/l (titanium content 2.7 %)
- Aluminium alkyl: TEA Al/Ti = 5
- Donor: CHMMS, Al/Don = 10
- Catalyst diluent: pentane 5 ml/g cat

5

1/3 of the donor and the cocatalyst were reacted for 5 min. and fed into the reactor. The rest of the donor and the cocatalyst was mixed in pentane with the catalyst and they were allowed to stay in contact for 10 min. The catalyst complex was fed into the reactor with a bottom pipe under the surface of the wax and it was agitated with an anchor agitator at a rotational speed of 300 rpm.

10

Agitation was continued for 15 min. and then the rotational speed was raised to 600 rpm and propylene feed (5 g/g cat) was commenced at a partial pressure of 4.0 bar. The temperature was maintained at exactly 30 °C. Prepolymerization was continued for 40 min until all the premonomer had reacted.

15

The product was removed from the reactor via a valve and via a 2 mm pipe fitted to the bottom of the reactor vessel and collected into sample bottles. The viscosity of the catalyst wax was somewhat decreased [0.5 Ns/m<sup>2</sup> (500 cP)] during prepolymerization, but not significantly as far as settling was concerned. A 1.0 litre glass sample vessel filled with the product was monitored for half a year and the product was found to remain non-sedimented and also otherwise in unchanged condition.

#### **Test polymerization results**

20

Using the prepolymerized catalyst wax a test polymerization was carried out by using the above-described standard method one (1) day and five (5) months after the prepolymerization. The purpose of the prolonged test period was to ascertain whether the isotacticity of the polymer decreases upon extended storage. The polymerization product comprised regularly shaped spherical particles of uniform size, which shows that pre-polymerization had been homogeneous.

25

Table 1.

Slurry-polymerization of propylene for 4.0 h at 70 °C		
	1 day after prepolymerization	5 months after prepolymerization
Aktivity	15.3 kg/g cat	15.8 kg/g cat
Isotactivity	97.9 %	97.3 %
Isotact.index	96.8 %	96.1 %
Melt index	4.7 (2.16 kg)	3.4 (2.16 kg)
Fines	4.2 % (d < 1.00 mm)	4.0 % (d < 1.00 mm)
Bulk density	0.46 g/cm <sup>3</sup>	0.46 g/cm <sup>3</sup>

40

#### **EXAMPLE 2**

##### **Prepolymerization of a MgCl<sub>2</sub> based catalyst with 4-methyl-1-pentene on laboratory scale**

45

The process described in Example 1 was followed using the following starting compounds:

50

- Polyethylene wax (PAO 6 cSt + 4.0 p-% PE-wax) viscosity 6.5 Ns/m<sup>2</sup> (6500 cP)
- Aluminium alkyl: TIBA, Al/Ti = 5
- Donor: MTBE (tert-methyl butyl ether) Al/Don = 10
- 4M1P (5 g/g cat), which was gradually fed into the reactor in liquid form

All prepolymer was consumed in the reaction so it did not cause any change of viscosity.

#### **Test polymerization results**

55

The prepolymerized catalyst wax was test polymerized according to the standard method. The polymer particles was regularly spherical and of uniform size.

Table 2.

Slurry-polymerization of propylene for 4.0 h at 70 °C		
	1 day after prepolymerization	5 months after prepolymerization
Activity	14.3 kg / g cat	14.1 kg / g cat
Isotacticity	98.2 %	97.9 %
Isotact.index	96.8 %	96.5 %
Melt index	5.7 (2.16 kg)	5.4 (2.16 kg)
Fines	5.2 % (d < 1.00 mm)	5.6 % (d < 1.00 mm)
Bulk density	0.42 g/cm <sup>3</sup>	0.46 g/cm <sup>3</sup>

**EXAMPLE 3****Prepolymerization of a MgCl<sub>2</sub> based catalyst with propylene on pilot plant scale**

A PP catalyst of Ziegler-Natta type was prepolymerized in a 10 dm<sup>3</sup> pilot plant reactor. A polyethylene wax was used as medium, the wax containing 4.0 wt-% of polyethylene in PAO oil. The wax was prepared in the prepolymerization reactor as described above and its temperature was lowered to 20 °C, a viscosity of 7 Ns/m<sup>2</sup> (7,000 cP) being obtained.

Reagents used:

- Catalyst amount: 17.3 g/l (titanium content 2.7 %)
- Aluminium alkyl: TEA, Al / Ti = 5
- Donor: CHMMS, Al/Don = 10

The cocatalyst and the donor were separately fed into the reactor so that they were in contact for 15 min under agitation. The dry catalyst was fed into the reactor (with a bottom pipe into the wax) and the mixture was mixed for 15 min before premonomer feed. Propylene was slowly fed (5 g/g cat) into the reactor such that its partial pressure was 300 kPa (3.0 bar) [+ nitrogen 100 kPa (1.0 bar)]. The propylene feed into the reactor was continued for 105 min, the total prepolymerization time being 120 min. During the first hour, the temperature was maintained in the range of 25 to 30 °C. During the second hour the temperature was kept at 30 to 35 °C.

When the catalyst is dried from liquid medium, lumps are formed. None of these were found during wax prepolymerization.

The wax prepolymerized catalyst was tested and later run on PILOT scale in a LOOP reactor.

Test polymerization results	
Aktivity	13.0 kg/g cat
Isotacticity	98.3 %
Isotact.index	97.1 %
Melt index	4.3 (2.16 kg)
Fines	3.6 % (d < 1.00 mm)
Bulk density	0.45 g/cm <sup>3</sup>

**EXAMPLE 4****Prepolymerization of a MgCl<sub>2</sub> based catalyst with propylene on pilot plant scale**

The test was carried out as Example 3, but prepolymerization was continued with vinyl cyclohexane (3 g VCH/g cat). The prepolymerization time with VCH was 6.0 hours, the temperature being 38 °C at low mixing speed.

Test polymerization results	
Activity	13.4 kg/g cat

(continued)

5

Test polymerization results	
Isotacticity	98.0 %
Isotact.index	96.9 %
Melt index	4.2 (2.16 kg)
Fines	4.0 % (d < 1.00 mm)
Bulk density	0.46 g/cm <sup>3</sup>

10

**EXAMPLE 5****Prepolymerization of a MgCl<sub>2</sub> based catalyst with propylene and vinyl cyclohexane on pilot plant scale**

15

The method described in Example 3 was repeated with the difference that

- the amount of propylene was 3 g/g cat and
- 1,8-Cineole (Al/Don = 10) was used as donor

20

25

Test polymerization results:	
Activity	14.4 kg/g cat
Isotacticity	97.8 %
Isotact.index	96.9 %
Melt index	4.5 (2.16 kg)
Fines	3.2 % (d < 1.00mm)
Bulk density	0.45 g/cm <sup>3</sup>

30

**Claims**

1. A prepolymerized catalyst composition suitable for use in the polymerization of alpha-olefins, comprising a prepolymerization medium comprising a procatalyst composition comprising a transition metal, the procatalyst composition being prepolymerized with a prepolymerization monomer in the presence of a viscous substance, the viscosity of the viscous substance being such that the prepolymerization medium viscosity is at least 1 Ns/m<sup>2</sup> (1,000 cP).
2. The catalyst composition according to claim 1, wherein said transition metal is deposited on a suitable support.
3. The catalyst composition according to claim 1 or 2, wherein said viscous substance is inert to the components of said procatalyst composition, and has a viscosity sufficiently high that the resulting prepolymerized catalyst does not settle.
4. The catalyst composition according to any of claims 1 to 3, wherein said viscous substance consists essentially of a wax.
5. The catalyst composition according to claim 4, wherein said wax consists essentially of a polyolefin wax.
6. The catalyst composition according to claim 5, wherein said polyolefin wax consists essentially of a polyethylene wax, having a viscosity in the range of 1 to 15 Ns/m<sup>2</sup> (1,000 to 15,000 cP), preferably in the range of 4 to 10 Ns/m<sup>2</sup> (4,000 to 10,000 cP).
7. The catalyst composition according to claim 5, wherein said wax consists essentially of an atactic polypropylene wax having a viscosity in the range of 1 to 15 Ns/m<sup>2</sup> (1,000 to 15,000 cP), preferably in the range of 4 to 10 Ns/m<sup>2</sup> (4,000 to 10,000 cP).
8. The catalyst composition according to claim 5, wherein said polyolefin wax consists essentially of liquid poly-alpha-

olefin mixed with 1 to 25 % polyethylene.

9. The catalyst composition according to claim 5, wherein said polyolefin wax consists essentially of a liquid poly-alpha-olefin mixed with 1 to 25 % of atactic polypropylene.

5       10. The catalyst composition according to any of the previous claims, wherein said prepolymerization monomer is selected from the group consisting of ethylene, propene, butene, 4-methyl-1-pentene, vinylcyclohexane, and mixtures thereof.

10      11. The catalyst composition according to claim 1, wherein said procatalyst composition was prepolymerized with a plurality of prepolymerization monomers.

15      12. A process for preparing a prepolymerized catalyst composition suitable for use in the polymerization of alpha-olefins, comprising

15           (a) forming a procatalyst composition by depositing a transition metal compound on a suitable support;  
              (b) adding said procatalyst composition to a viscous substance;  
              (c) prepolymerizing said procatalyst composition with a prepolymerization monomer in the presence of said viscous substance to provide a prepolymerization medium and so to obtain said prepolymerized catalyst composition, the viscosity of the viscous substance being such that the viscosity of the prepolymerization medium is at least 1 Ns/m<sup>2</sup> (1,000 cP)

- 20       13. The process according to claim 12, wherein said prepolymerizing step (c) comprises:

25           (1) preparing a wax having a viscosity in the range of 4 Ns/m<sup>2</sup> to 10 Ns/m<sup>2</sup> (4,000 to 10,000 cP) in a reaction vessel,  
              (2) maintaining the temperature of said wax in the range of 10 to 40 °C;  
              (3) mixing a cocatalyst for said procatalyst composition and an electron donor with said wax to produce a cocatalyst-containing wax composition;  
              (4) adding said procatalyst composition and said prepolymerization monomer to said cocatalyst-containing wax; and  
              (5) prepolymerizing said procatalyst composition and said prepolymerization monomer until said prepolymerization monomer has been consumed.

35       14. The process according to claim 12 or 13, further comprising agitating at least a portion of said viscous substance, and wherein said adding of said procatalyst composition occurs in said agitated portion.

- 40       15. The process according to any of claims 12 - 14, wherein said adding step (b) comprises:

40           (1) mixing a portion of a cocatalyst for said procatalyst composition with an electron donor and said procatalyst composition in an inert solvent to produce a slurry of said procatalyst composition;  
              (2) mixing the remaining portion of said cocatalyst into said viscous substance;  
              (3) agitating said cocatalyst-containing viscous substance; and  
              (4) mixing said slurry with said cocatalyst-containing viscous substance under agitation.

45       16. The process according to any of claims 12 - 15, wherein said prepolymerization monomer is present in an amount of from 0.01 to 50, preferably from 0.1 to 10 parts by weight, based upon the weight of said transition metal in said procatalyst composition.

50       17. The process according to any of claims 12 - 16, wherein said viscous medium consists essentially of a liquid poly-alpha-olefin mixed with 1 to 25 % by weight of either polyethylene or atactic polypropylene.

55       18. The process according to any of claims 12 - 17, wherein said prepolymerization is initiated using an initial prepolymerization monomer and continued or terminated using a different prepolymerization monomer.

- 55       19. The process according to claim 18, wherein said prepolymerization is initiated using propylene and continued or terminated using vinylcyclohexane.

20. A process for polymerizing alpha-olefins using the prepolymerized catalyst composition according to claim 1, comprising contacting said prepolymerized catalyst composition with an alpha-olefin monomer under conditions sufficient to produce a polymer.
- 5      21. The process according to claim 20, wherein said alpha-olefin is propylene or ethylene.

**Patentansprüche**

- 10     1. Vorpolymerisierte Katalysatorzusammensetzung, die zum Einsatz bei der Polymerisation von Alpha-Olefinen geeignet ist und ein Vorpolymerisationsmittel umfassend eine Prokatalysatorzusammensetzung mit einem Übergangsmetall umfaßt, wobei die Prokatalysatorzusammensetzung mit einem Vorpolymerisationsmonomer in Gegenwart einer viskosen Substanz vorpolymerisiert wird, wobei die viskose Substanz eine solche Viskosität aufweist, daß die Viskosität des Vorpolymerisationsmittels bei mindestens 1 Ns/m<sup>2</sup> (1.000 cP) liegt.
- 15     2. Katalysatorzusammensetzung nach Anspruch 1, wobei das Übergangsmetall auf einem geeigneten Träger abgelagert ist.
- 20     3. Katalysatorzusammensetzung nach Anspruch 1 oder 2, wobei die viskose Substanz gegenüber den Komponenten der Prokatalysatorzusammensetzung inert ist und eine genügend hohe Viskosität aufweist, daß der resultierende vorpolymerisierte Katalysator nicht sedimentiert.
- 25     4. Katalysatorzusammensetzung nach einem der Ansprüche 1 bis 3, wobei die viskose Substanz im wesentlichen aus einem Wachs besteht.
- 30     5. Katalysatorzusammensetzung nach Anspruch 4, wobei das Wachs im wesentlichen aus einem polyolefinen Wachs besteht.
- 35     6. Katalysatorzusammensetzung nach Anspruch 5, wobei das polyolefine Wachs im wesentlichen aus einem Polyethylenwachs mit einer Viskosität im Bereich von 1 bis 15 Ns/m<sup>2</sup> (1.000 bis 15.000 cP), vorzugsweise im Bereich von 4 bis 10 Ns/m<sup>2</sup> (4.000 bis 10.000 cP) besteht.
- 40     7. Katalysatorzusammensetzung nach Anspruch 5, wobei das Wachs im wesentlichen aus einem ataktischen Polypropylenwachs mit einer Viskosität im Bereich von 1 bis 15 Ns/m<sup>2</sup> (1.000 bis 15.000 cP), vorzugsweise im Bereich von 4 bis 10 Ns/m<sup>2</sup> (4.000 bis 10.000 cP) besteht.
- 45     8. Katalysatorzusammensetzung nach Anspruch 5, wobei das Polyolefinwachs im wesentlichen aus einem flüssigem Poly-Alpha-Olefin gemischt mit 1 bis 25 % Polyethylen besteht.
- 50     9. Katalysatorzusammensetzung nach Anspruch 5, wobei das Polyolefinwachs im wesentlichen aus einem flüssigen Poly-Alpha-Olefin gemischt mit 1 bis 25 % ataktischem Polypropylen besteht.
- 55     10. Katalysatorzusammensetzung nach einem der vorstehenden Ansprüche, wobei das Vorpolymerisationsmonomer aus Ethylen, Propen, Buten, 4-Methyl-1-Penten, Vinylcyclohexan oder Mischungen daraus besteht.
11. Katalysatorzusammensetzung nach Anspruch 1, wobei die Prokatalysatorzusammensetzung mit mehreren Vorpolymerisationsmonomeren vorpolymerisiert wurde.
12. Verfahren zur Herstellung einer vorpolymerisierten Katalysatorzusammensetzung geeignet zum Einsatz bei der Polymerisation von Alpha-Olefinen, umfassend
- (a) das Bilden einer Prokatalysatorzusammensetzung durch Sedimentieren einer Übergangsmetallverbindung auf einem geeigneten Träger;
- (b) das Addieren der Prokatalysatorzusammensetzung und einer viskosen Substanz;
- 55     (c) das Vorpolymerisieren der Prokatalysatorzusammensetzung mit einem Vorpolymerisationsmonomer in Gegenwart der viskosen Substanz zur Bereitstellung eines Vorpolymerisationsmittels und so zum Erhalt der vorpolymerisierten Katalysatorzusammensetzung, wobei die viskose Substanz eine solche Viskosität aufweist, daß die Viskosität des Vorpolymerisationsmittels mindestens 1 Ns/m<sup>2</sup> (1.000 cP) beträgt.

13. Verfahren nach Anspruch 12, wobei die Vorpolymerisationsstufe (c) umfaßt:

- (1) Herstellen eines Wachs mit einer Viskosität im Bereich von 4 Ns/m<sup>2</sup> bis 10 Ns/m<sup>2</sup> (4.000 bis 10.000 cP) in einem Reaktionsgefäß;
- 5 (2) Beibehalten der Temperatur des Wachs im Bereich von 10 bis 40 °C;
- (3) Mischen eines Kokatalysators für die Prokatalysatorzusammensetzung und eines Elektronendonators mit dem Wachs zur Herstellung einer Wachszusammensetzung enthaltend den Kokatalysator;
- (4) Addieren der Prokatalysatorzusammensetzung und des Vorpolymerisationsmonomers zu dem den Katalysator enthaltenden Wachs; und
- 10 (5) Vorpolymerisieren der Prokatalysatorzusammensetzung und des Vorpolymerisationsmonomers, bis das Vorpolymerisationsmonomer verbraucht ist.

14. Verfahren nach Anspruch 12 oder 13, weiter umfassend das Rühren mindestens eines Teils der viskosen Substanz, wobei das Addieren der Prokatalysatorzusammensetzung in dem gerührten Teil auftritt.

- 15 (15) 15. Verfahren nach einem der Ansprüche 12 - 14, wobei die Additionsstufe (b) umfaßt:

- (1) Mischen eines Teils des Kokatalysators für die Prokatalysatorzusammensetzung mit einem Elektronendonator und der Prokatalysatorzusammensetzung in einem inerten Lösungsmittel zur Bildung einer Prokatalysatorzusammensetzungssuspension;
- 20 (2) Mischen des restlichen Teils des Kokatalysators in die viskose Substanz;
- (3) Rühren der den Kokatalysator enthaltenden viskosen Substanz; und
- (4) Mischen der Suspension mit der den Kokatalysator enthaltenden viskosen Substanz unter Rühren.

- 25 (16) 16. Verfahren nach einem der Ansprüche 12 - 15, wobei das Vorpolymerisationsmonomer in einer Menge von 0,01 bis 50, vorzugsweise von 0,1 bis 10 Gewichtsteilen gegenwärtig ist, ausgehend von dem Gewicht des Übergangsmetalls in der Prokatalysatorzusammensetzung

- 30 (17) 17. Verfahren nach einem der Ansprüche 12 - 16, wobei die viskose Substanz im wesentlichen aus einem flüssigen Poly-Alpha-Olefin gemischt mit 1 bis 25 Gewichts-% Polyethylen oder ataktischem Polypropylen besteht.

- 35 (18) 18. Verfahren nach einem der Ansprüche 12 - 17, wobei die Vorpolymerisation durch Einsatz eines initiatorischen Vorpolymerisationsmonomers initiiert und durch Einsatz eines anderen Vorpolymerisationsmonomers fortgesetzt oder beendet wird

- 35 (19) 19. Verfahren nach Anspruch 18, wobei die Vorpolymerisation durch Einsatz von Propylen initiiert und durch Einsatz von Vinylcyclohexan fortgesetzt oder beendet wird.

- 40 (20) 20. Verfahren zur Polymerisation von Alpha-Olefinen durch Einsatz der vorpolymerisierten Katalysatorzusammensetzung nach Anspruch 1, umfassend die Berührung der vorpolymerisierten Katalysatorzusammensetzung mit einem Alpha-Olefinmonomer unter zur Herstellung eines Polymers ausreichenden Verhältnissen.

- 45 (21) 21. Verfahren nach Anspruch 20, wobei das Alpha-Olefin Propylen oder Ethylen ist.

#### **Revendications**

1. Composition de catalyseur pré-polymérisée utilisable dans la polymérisation d'alpha-oléfines, comprenant un milieu de pré-polymérisation comprenant une composition de pro-catalyseur comprenant un métal de transition, la composition de pro-catalyseur étant pré-polymérisée avec un monomère de pré-polymérisation en présence d'une substance visqueuse, la viscosité de la substance visqueuse étant telle que la viscosité du milieu de pré-polymérisation est d'au moins 1 Ns/m<sup>2</sup> (1.000 cP).
- 50 2. Composition de catalyseur suivant la revendication 1, dans laquelle ce métal de transition est déposé sur un support convenable.
- 55 3. Composition de catalyseur suivant les revendications 1 ou 2, dans laquelle cette substance visqueuse est inerte vis-à-vis des composants de cette composition de pro-catalyseur, et a une viscosité suffisamment élevée pour

que le catalyseur pré-polymérisé résultant ne décante pas.

4. Composition de catalyseur suivant l'une quelconque des revendications 1 à 3, dans laquelle cette substance visqueuse consiste essentiellement en une cire
5. Composition de catalyseur suivant la revendication 4, dans laquelle cette cire consiste essentiellement en une cire de polyoléfine.
10. Composition de catalyseur suivant la revendication 5, dans laquelle cette cire de polyoléfine consiste essentiellement en une cire de polyéthylène, ayant une viscosité comprise dans la gamme de 1 à 15 Ns/m<sup>2</sup> (1.000 à 15.000 cP), de préférence dans la gamme de 4 à 10 Ns/m<sup>2</sup> (4.000 à 10.000 cP).
15. Composition de catalyseur suivant la revendication 5, dans laquelle cette cire de polyoléfine consiste essentiellement en une cire de polypropylène atactique, ayant une viscosité comprise dans la gamme de 1 à 15 Ns/m<sup>2</sup> (1.000 à 15.000 cP), de préférence dans la gamme de 4 à 10 Ns/m<sup>2</sup> (4.000 à 10.000 cP).
20. Composition de catalyseur suivant la revendication 5, dans laquelle cette cire de polyoléfine consiste essentiellement en une poly(alpha-oléfine) liquide, mélangée avec 1 à 25% de polyéthylène.
25. Composition de catalyseur suivant la revendication 5, dans laquelle cette polyoléfine consiste essentiellement en une poly(alpha-oléfine) liquide, mélangée avec 1 à 25% de polypropylène atactique.
30. 10. Composition de catalyseur suivant l'une quelconque des revendications précédentes, dans laquelle ce monomère de pré-polymérisation est choisi dans le groupe consistant en éthylène, propène, butène, 4-méthyl-1-pentène, vinylcyclohexane et mélanges de ceux-ci.
35. 11. Composition de catalyseur suivant la revendication 1, dans laquelle cette composition de pro-catalyseur est pré-polymérisée avec plusieurs monomères de pré-polymérisation.
40. 12. Procédé pour préparer une composition de catalyseur pré-polymérisée utilisable dans la polymérisation d'alpha-oléfines, comprenant :
  - (a) la formation d'une composition de pro-catalyseur par dépôt d'un composé de métal de transition sur un support convenable;
  - (b) l'addition de cette composition de pro-catalyseur à une substance visqueuse;
  45. (c) la pré-polymérisation de cette composition de pro-catalyseur avec un monomère de pré-polymérisation en présence de cette substance visqueuse pour fournir un milieu de pré-polymérisation et obtenir ainsi cette composition de catalyseur pré-polymérisée, la viscosité de la substance visqueuse étant telle que la viscosité du milieu de pré-polymérisation est d'au moins 1 Ns/m<sup>2</sup> (1.000 cP).
45. 13. Procédé suivant la revendication 12, dans lequel cette étape (c) de pré-polymérisation comprend :
  - (1) la préparation d'une cire ayant une viscosité comprise dans la gamme de 4 Ns/m<sup>2</sup> à 10 Ns/m<sup>2</sup> (4.000 à 10.000 cP) dans un récipient de réaction;
  - (2) le maintien de la température de cette cire dans la gamme de 10°C à 40°C;
  - (3) le mélange d'un co-catalyseur pour cette composition de pro-catalyseur d'un électrodonneur avec cette cire afin de produire une composition de cire contenant un co-catalyseur;
  - (4) l'addition de cette composition de pro-catalyseur et de ce monomère de pré-polymérisation à cette cire contenant un co-catalyseur; et
  50. (6) la pré-polymérisation de cette composition de pro-catalyseur et de ce monomère de pré-polymérisation jusqu'à consommation de ce monomère de pré-polymérisation.
55. 14. Procédé suivant les revendications 12 ou 13, comprenant de plus l'agitation d'au moins une partie de cette substance visqueuse et dans lequel cette addition de cette composition de pro-catalyseur a lieu dans cette partie agitée.
15. Procédé suivant l'une quelconque des revendications 12 à 14, dans lequel cette étape d'addition (b) comprend :
  - (1) le mélange d'une partie d'un co-catalyseur pour cette composition de pro-catalyseur avec un électrodon-

neur et cette composition de pro-catalyseur dans un solvant inerte pour produire une bouillie de cette composition de pro-catalyseur;

(2) le mélange de la partie restante de ce co-catalyseur dans cette substance visqueuse;

(3) l'agitation de cette substance visqueuse contenant un co-catalyseur;

5 (4) le mélange avec agitation de cette bouillie avec cette substance visqueuse contenant un co-catalyseur.

16. Procédé suivant l'une quelconque des revendications 12 à 15, dans lequel ce monomère de pré-polymérisation est présent en une quantité de 0,01 à 50, de préférence de 0,1 à 10, parties en poids, par rapport au poids de ce métal de transition dans cette composition de pro-catalyseur.

10 17. Procédé suivant l'une quelconque des revendications 12 à 16, dans lequel ce milieu visqueux consiste essentiellement en une poly(alpha-oléfine) liquide mélangée avec 1 à 25% en poids, soit de polyéthylène, soit de polypropylène atactique.

15 18. Procédé suivant l'une quelconque des revendications 12 à 17, dans lequel cette pré-polymérisation est initiée par utilisation d'un monomère de pré-polymérisation initial et poursuivie ou terminée par utilisation d'un monomère différent de pré-polymérisation.

20 19. Procédé suivant la revendication 18, dans lequel cette pré-polymérisation est initiée par utilisation de propylène et poursuivie ou terminée par utilisation de vinylcyclohexane.

25 20. Procédé pour la polymérisation d'alpha-oléfines utilisant la composition de catalyseur pré-polymérisée suivant la revendication 1, comprenant la mise en contact de cette composition de catalyseur pré-polymérisée avec une alpha-oléfine monomère dans des conditions suffisantes pour produire un polymère.

21. Procédé suivant la revendication 20, dans lequel cette alpha-oléfine est le propylène ou l'éthylène.

30

35

40

45

50

55